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 (54) [Title of the Invention]

## GLASS FIBER SIZING AGENTS AND GLASS FIBER CLOTH

## (57) [Abstract]

[Object] To prevent the formation of fuzz in the processing of glass fiber and to make the removal of oil by heat from the finished glass cloth unnecessary by treating the glass fiber with the sizing agent of the inven-



tion. To improve the adhesion between a laminate and copper foil by preventing the formation of fuzz and the heat setting of the glass cloth.

[Constitution] To produce a bound glass fiber strand by applying to the glass fiber during spinning a sizing agent that contains polyvinylpyrrolidone, a water-soluble epoxy resin amine addition product, and a silane coupling agent, and then drying. To produce glass cloth by making the strand into glass fiber yarn then weaving said yarn. To use the glass cloth to produce a laminate by impregnating it with an epoxy resin without de-oiling or after de-oiling by washing with water.

[Scope of the Patent Claim(s)]

[Claim 1] Primary sizing agent for glass fiber, characterized in that its essential components are polyvinylpyrrolidone, a water-soluble epoxy resin amine addition product, and a silane coupling agent.

[Claim 2] Sizing agent according to Claim 1, which contains 1-10 weight% of polyvinylpyrrolidone as solids and where said polyvinylpyrrolidone has a K-value of 15-120 and a molecular weight of 10,000-1,500,000.

[Claim 3] Sizing agent according to Claim 1, which contains 0.5-8 weight% of a water-soluble epoxy resin amine addition product as solids and where said water-soluble epoxy resin amine addition product has an epoxy equivalent weight of 180-2,100 and a molecular weight of 300-2,900.

[Claim 4] Glass fiber cloth woven with a glass fiber yarn coated with 0.1-3.0 weight% of the sizing agent of Claim 1.

[Claim 5] Glass fiber cloth according to Claim 4, in which the coating weight of sizing agent is adjusted to 0.1-0.3 weight% by de-oiling by the well-known water-washing de-oiling method.

[Detailed Description of the Invention]



[0001]

[Field of Industrial Application] The present invention pertains to the production of glass fiber cloth of the type used to produce copper-lined laminates, etc. In more detail, the present invention pertains to glass fiber sizing agents that go into the making of glass fiber cloth that in turn can be used to produce laminates with excellent adhesion strength with copper foil and that have excellent chemical resistance; glass fiber yarns that incorporate said sizing agent; and glass fiber cloth.

[0002]

[Conventional Techniques] Generally, laminates using glass fiber cloth as a reinforcing base material have excellent mechanical properties, electrical properties, heat resistance, and chemical resistance. Because of these properties, glass fiber cloth is mainly used as a reinforcing material for sheets of electrical insulation or copper-lined laminates that are used in computers and OA instruments. Conventional glass fiber cloth is produced as follows: First, molten glass is extruded from a large number of orifices in a platinum alloy extrusion plate and spun at high speed, while a primary sizing agent is simultaneously applied to the glass fiber bundle for the purpose of helping to produce an assembled glass fiber bundle and to provide protection. A glass fiber yarn produced by giving said fiber bundle a "twist" is then used as the warp and weft in weaving a glass fiber cloth. Next, a treatment known as de-oiling is carried out in order to remove the sizing agent that has adhered to the surface of the glass fibers. For the de-oiling treatment, a method usually called heat de-oiling is used, which is widely practiced, where the sizing agent is removed from the glass fiber cloth by thermally decomposing its constituents by heating at high temperatures. The de-oiled glass



fiber cloth is given a surface treatment with a silane coupling agent in order to increase the bond strength between the glass fiber and the matrix resin, then it is used as a reinforcing material.

[0003] In recent years, copper-lined laminates for use in computers and OA instruments have been made smaller in shape, and the circuits to be assembled on the top of these laminates are being produced in increasingly higher densities and with much greater precision. In the process of producing a circuit on a copper-lined laminate, treatments with various chemicals are carried out. For example, the adhesion between the copper foil and the laminate tends to be decreased by treatment with a chlorine-based solvent such as methylene chloride in a resist stripping or washing process. The widths of circuits formed by etching the copper foil are being made smaller and smaller, which in turn increases the likelihood of weakening the adhesion, as the density of these circuits becomes greater. Paralleling this trend is a strong demand for further improvement in the reliability of printed circuits.

[0004] Measures to control this problem include improvement in the adhesion of the copper foil and the chemical resistance by improving the performance of the glass fiber cloth and making the surface of the copper-lined laminate smoother. Existing problems which tend to weaken the adhesion of the copper foil and/or lower the chemical resistance of the copper-lined laminate include the unevenness due to the presence of fine glass fiber yarn at the surface of the laminate of the copper-lined laminate and fuzz from the glass cloth. These difficulties are thought to be due to the heat de-oiling treatment that is applied to the glass fiber cloth used in the copper-lined laminate in order to remove the sizing agent adhering to the surface of the glass fibers by heating. In this heat de-oiling treatment, high heating tempera-



tures are applied for a long time, for example 400°C for 20 hours. Accordingly, the warp and weft become set by heat and the glass fibers making up the fiber bundles are damaged. At the intersection of the warp and weft, mobility is especially low in response to an external force, and this causes unevenness.

[0005] As a result, the glass fiber bundles making up the glass fiber yarn cannot be readily flattened out in the resin impregnation and pressing process, consequently the area where the warp crosses the weft in the glass fiber cloth becomes raised and thus the surface of the laminate becomes uneven. To prevent this, the cloth has to be woven with a glass fiber yarn that has been treated with a sizing agent and that does not require de-oiling. Moreover, when weaving in an air jet loom, fuzz (which is another cause of laminate surface unevenness) is produced as the warp is struck by a "reed" and an air guide thus cutting some of the filaments in the yarn which is used as the warp. Also, when driving in the weft with a high-speed air jet, the powerful stream of air blown on the yarn may cut some of the weft threads.

[0006] As a means of solving these problems encountered in the weaving of glass fiber yarn and the problems encountered in molding the resulting glass fiber cloth into a laminate, Japanese Kokai No. 6[1994]-160,778 and Japanese Kokai No. 6[1994]-274,265 disclose, respectively, a glass fiber yarn that does not require de-oiling by heating and a glass fiber yarn that displays good resistance to the formation of fuzz and good weaving properties. However, the first glass fiber yarn requires two treatment processes with a primary sizing agent and a secondary sizing agent before weaving, and with the second glass fiber yarn, the "travel" efficiency declines when the yarn is woven on an air jet loom, because the water-soluble epoxy resin used both as a

film-former and a binder causes the surface of the yarn to become sticky. Furthermore, when PVP is used as the sole film-former, the cost is driven up because it is not easily bundled and produces fuzz easily during weaving, which means that large quantities of it must be used.

[0007]

[Problems to be Solved by the Invention] The object of the present invention is to provide a glass fiber sizing agent which can be used in the production of copper-lined laminates with improved adhesion of the copper foil and improved chemical resistance, and that do not require de-oiling by heating; a glass fiber yarn produced with the use of said sizing agent; and glass fiber cloth produced from this glass fiber yarn.

[0008]

[An Approach to solving the Problems] The present inventor discovered that, if polyvinylpyrrolidone (abbreviated as PVP) and a water-soluble epoxy amine addition product (abbreviated as SEPA) are used in combination as a glass fiber yarn sizing agent, a yarn with good weaving properties with no need for heat de-oiling can be produced. In addition, a printed wiring board with improved adhesion of the copper foil and chemical resistance of a copper-lined laminate can be produced when the glass fiber cloth produced is used to make up the copper-lined laminate. It was this discovery that led to the development of the present invention.

[0009] It is desirable for the K-value of the PVP, which is the first essential component of the present invention, to be 15-120 (molecular weight = 10,000-1,500,000), and particularly 30-90 (molecular weight = 40,000-630,000). If the K-value is less than 15, the film-forming ability declines to some extent and the weaving properties deteriorate. With values



of more than 120, on the other hand, the solubility in the binder tends to decrease. The amount of sizing agent to be added is in the range of 1-10 weight%, and preferably in the range of 5-7 weight%.

[0010] The water-soluble epoxy resin amine addition product (SEPA) which is the second essential component of the sizing agent of the present invention and is the reaction product of an epoxy resin and a hydroxyl group-containing amine compound, is a product obtained by reacting an epoxy resin with an epoxy equivalent weight of 180-2,100 with a hydroxyl group-containing amine compound.

[0011] The epoxy resin which is a starting material of the SEPA may be either the bisphenol or novolac type, but products with epoxy equivalent weights of 180-2,100 and molecular weights of 350-2,900 are preferred, as mentioned above. As the hydroxyl group-containing amine compound to be reacted with the epoxy resin, a hydroxyl group-containing primary amine or secondary amine is preferred; specific examples include monoethanolamine, mono-*n*-propanolamine, monoisopropanolamine, monobutanolamine, diethanolamine, methylaminoethanol, ethylaminoethanol, and dipropanolamine.

[0012] For example, an epoxy resin and diethanolamine can be reacted in the following manner. First, a solvent is added so as to adjust the amount of epoxy resin to about 50 weight%, then this mixture is heated until the boiling point of the solvent is reached. Solvents that can be used are those that will dissolve the epoxy resin and hydroxyl group-containing amine compound; for example, diacetone alcohol and isopropyl Cellosolve can be used. Next, the hydroxyl group-containing amine compound is added dropwise to the epoxy resin solution with which it reacts. When the reaction is complete, the solution is cooled to an ordinary temperature to obtain a SEPA, which is an essen-



tial component of the sizing agent of the present invention. In this reaction, the epoxy rings at both ends of the epoxy resin each preferably react with the hydroxyl group-containing amine compound. In this way, a SEPA with hydroxyl groups at both ends that come from the aforesaid amine compound can be obtained.

[0013] When the weaving properties were examined for various types of SEPA, a product using a bisphenol A-type epoxy resin with a molecular weight of 350-400 and diethanolamine showed good results. The solids content of the SEPA in the sizing agent is preferably 0.5-8 weight%. With less than 0.5 weight%, the glass fibers cannot be easily bundled and fuzz forms more readily, thus the weaving properties are adversely affected. With a solids contents of more than 8 weight%, the bundling ability is so strong that the yarn cannot be carried easily on air and the travel distance is shortened when weaving on an air jet loom. In other words, the weaving properties are adversely affected.

[0014] The silane coupling agent which is the third essential component can be epoxysilane, vinylsilane, methacrylsilane, aminosilane, or mercaptosilane, but any silanes can be used with no particular limits as long as they contribute to the bonding of the glass fiber and the resin. Apart from the essential components, lubricants, surfactants, antistatic agents, etc., can be incorporated, as needed, in the sizing agent, in the same way as with conventional sizing agents. These additives can be used in amounts that work best, so there is no need to set any particular limits.

[0015] 0.1-3.0 weight%, and preferably 0.4-0.7 weight%, as solids, of the sizing agent used in the present invention is preferably coated on the glass fiber yarn. With less than 0.1 weight%, the yarn is likely to come





apart and fuzz will form easily. With more than 3.0 weight%, the bundling ability becomes so strong that the weft cannot be carried easily on the air jet stream. And in some cases, the weft does not even pass through the entire width of the cloth. A glass fiber cloth woven with the yarn produced by the present invention can be used directly in the production of copper-lined laminates. Also usable are products which have been de-oiled, as needed, by the well-known methods which remove the sizing agent by washing the glass fiber cloth with water; for example, a method which vibrates the cloth in a water tank or a method which sprays the cloth with high-pressure water. In a cloth de-oiled by washing with water, the silane coupling is bound to the surface of the glass fibers and any extra sizing agent is washed away. As a result, the fibers of the glass fiber yarn spread more easily, and physical properties such as the peel strength of the copper foil of the laminate and the chemical resistance improve. The effect of de-oiling by washing with water appears when the amount of remaining sizing agent in the form of solids is adjusted to 0.5 weight% or less, and preferably to 0.1-0.3 weight%. Furthermore, a glass cloth de-oiled by washing with water may be surface treated with a silane coupling agent.

[0016]

[Effect of the Invention] A glass fiber sizing agent of the present invention uses both PVP with a molecular weight of 10,000-1,500,000 and a SEPA obtained by reacting an epoxy resin with an epoxy equivalent of 1,800-2,100 with a hydroxyl group-containing amine compound in combination, and hence a flexible and strong film forms after the sizing agent is dried, which provides a glass fiber yarn with little stickiness that can be gathered together easily. As a result, a glass fiber yarn which does not form fuzz



easily and has very good weaving properties can be obtained for use especially in high-speed air jet looms. Moreover, cloth woven with the glass fiber yarn coated with the sizing agent of the present invention requires no heat de-oiling over a long period of time, so that the glass fiber does not become heat set. Because of this, the glass fibers are quite mobile when preregs impregnated with a resin are stacked and press molded, hence the surface of the molded product can be made smooth, and when a copper-lined laminate is prepared, the bonding state with the copper foil and the chemical resistance are improved. Actual examples will now be given to better describe the present invention in more detail, however, it should be understood that the present invention is not in any way limited to the following actual examples. "% in the actual examples is based on weight unless otherwise specified.

[0017]

[Actual Examples]

Actual Example 1

A yarn of 67.5 g/1,000 m was produced with the use of a glass fiber bundle obtained by spinning an E glass composition at 1,260°C and at a rate of 3,000 m/min with the use of a die for glass fiber that had an extrusion plate with 2,000 orifices, and applying 0.7% as solids of a primary sizing agent consisting of 7.0% as solids of polyvinylpyrrolidone (K = 30) (produced by Wako Pure Chemicals Co., Ltd.) as a film-former, 2.0% as solids of a product obtained by adding one mole of diethanolamine (produced by Wako Pure Chemicals Co., Ltd.) to Epikote 828 (produced by Shell Chemical Co.) with a molecular weight of 380 and an epoxy equivalent of 190 as a binder, 0.5% as solids of epoxysilane A-187 (produced by Nippon Unicar Co., Ltd.) as a surface treatment agent, 0.5% as solids of butyl stearate emulsion as a lubricant, with the



remaining 90% consisting of water.

[0018] A cloth with a warp density of 44 yarns/25 mm and a weft density of 32 yarns/25 mm was woven with the above-mentioned yarn and prepregs were prepared by impregnating the cloth with an FR4-type epoxy resin varnish with a resin content of 47%. Five prepregs were laminated, both sides of the laminate were overlaid with a piece of copper foil 18- $\mu$ m thick, and the whole assembly was press molded with a heat press (heating temperature = 170°C, pressure = 30 kg/cm<sup>2</sup>, heating time = 30 min) to obtain a copper-lined laminate 0.55-mm thick.

[0019] The coating weight of the sizing agent used on the glass fiber yarn and glass cloth was measured by the following method.

(1) Coating Percentage of the Sizing Agent

More than 1 g of a test specimen was collected and dried at 110  $\pm$  5°C for more than 1 hour. Next, it was placed in a desiccator and cooled to room temperature, and then weighed. This specimen was then heated to constant weight in a muffle furnace kept at 625  $\pm$  20°C. It was then placed in a desiccator and cooled to room temperature, and finally it was weighed. The coating percentage was calculated by the following equation:  $C = (M1 - M2)/M1 \times 100$ , where  $C$  is the sizing agent coating percentage of the test specimen in weight%,  $M1$  is the weight of the test specimen after drying, and  $M2$  is the weight of the test specimen after heating. The prepared laminate was then evaluated under the conditions below. The results are shown in Table 1.

(1) Evaluation of the Peel Strength of the Copper Foil

A test specimen was prepared in accordance with JIS C 6481 and the peel strength was measured.

(2) Evaluation of the Chemical Resistance (to methylene chloride).



A test specimen was prepared in accordance with JIS C 6481 and dipped in boiling methylene chloride for 30, 60, and 90 minutes. The test specimens were then examined by visual inspection for any changes in appearance.

[0020]

### (3) Evaluation of Soldering Heat Resistance

The copper foil of the prepared copper-lined laminate was removed by etching with a ferric chloride solution and the remainder was cut into 4 cm x 4 cm pieces which were treated at 133°C for 60, 90, and 120 minutes in a pressure cooker. The resulting test specimens were dipped in molten solder at 260°C for 20 seconds and then checked for the presence of swelling.

[0021]

#### Actual Example 2

The operating procedure was the same as in Actual Example 1, except that the PVP content of the sizing agent of Actual Example 1 was adjusted to 5%.

#### Actual Example 3

The operating procedure was the same as in Actual Example 1, except that the coating weight of the sizing agent was adjusted to 0.2% by washing the glass fiber cloth woven according to Actual Example 1 with water for 30 seconds in an ultrasonic cleaning tank.

[0022]

#### Comparison Example 1

A glass fiber cloth woven according to Actual Example 1 was heat cleaned at 400°C for 20 hours to remove the binder solids adhering to the glass fiber. The resulting glass fiber cloth was dipped in a solution containing an epoxy-silane hydrolysis solution prepared so as to incorporate 1.0% as solids of epoxysilane (A-187 produced by Nippon Unicar Co., Ltd.) in the glass fiber



cloth, which was then wrung out and dried. The rest of the procedure was the same as in Actual Example 1.

[0023]

Comparison Example 2

The operating procedure was the same as in Actual Example 1, except that a sizing agent of the following composition, i.e., a type in common use, was used in place of the primary sizing agent of Actual Example 1.

Binder: aliphatic polyurethane emulsion, 2.0% solids.

Surface Treatment Agent: epoxysilane A-187 (produced by Nippon Unicar Co., Ltd.), 0.3% solids.

Lubricant: butyl stearate, 0.5% solids.

Water: 97.2%.

(Table 1)

TABLE 1. KEY: (a) Actual Example .... ; (b) Comparison Example .... ; (c) peel strength, kg/cm<sup>2</sup>; (d) chemical resistance; (e) soldering heat resistance; (f) test item; (g) evaluation; (h) no problems = "O"; (i) some degradation = "Δ"; (j) degraded = "X"; (k) small amount of swelling = "Δ"; and (l) large amount of swelling = "X".

		実施例1 (a)	実施例2 (a)	実施例3 (a)	比較例1 (b)	比較例2 (b)
	引剥がし強度 (c) (kg/cm <sup>2</sup> )	1.45	1.45	1.50	1.30	1.30
耐薬品性 (d)	30min	O	O	O	O	O
	45	O	O	O	Δ	Δ
	60	O	O	O	X	X
半田耐熱性 (e)	60min	O	O	O	O	O
	90	O	O	O	Δ	Δ
	120	Δ	Δ	Δ	X	X

(f) 試験項目 (g) 評価 (h) 評価 (g)  
 (d) 耐薬品性 (h) 問題なし : O (e) 半田耐熱性 (h) 問題なし : O  
 (i) 若干劣化 : Δ フクレ小 : Δ (k)  
 (j) 劣化 : X フクレ多 : X (l)



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WPI Accession No: 97-256154/199723

Preparation of mica sheet with good electrical insulating properties -  
by dispersing synthetic fluorine micas and micro-glass fibres in water,  
adding flocculant, diluting and paper making.

Patent Assignee: MITSUBISHI PAPER MILLS LTD (MITY )

Number of Countries: 001 Number of Patents: 001

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Main IPC	Week
JP09087992	A	19970331	95JP-0240395	A	19950920	D21H-013/44	199723 B

Priority Applications (No Kind Date): 95JP-0240395 A 19950920

Patent Details:

Patent	Kind	Lan	Pg	Filing Notes	Application	Patent
JP09087992	A					999

Abstract (Basic): JP 9087992 A.

Preparation of a mica sheet comprises dispersing synthetic fluorine micas and micro-glass fibres in water, forming an aggregate of the synthetic fluorine micas and micro-glass fibres by adding flocculant in the aqueous dispersion, diluting concentration of the solid of the aggregate to 0.01-2% and making paper using the diluted liquid with wet system paper making method. Also claimed is preparation of a mica sheet which comprises dispersing synthetic fluorine micas in water, forming an aggregate of the synthetic fluorine micas by adding a flocculant in the aqueous dispersion, and then mixing micro-glass fibres in the aggregate, diluting concentration of the solid to 0.01-2%, and making paper using the diluted liquid with wet system paper making method.

ADVANTAGE - The mica sheet has good electrical insulating property, heat resistance, mechanical strength and uniformity.

Dwg.0/0

Derwent Class: A85; F09; X12

International Patent Class (Main): D21H-013/44

International Patent Class (Additional): B29C-067/02; D21H-013/40;

H01B-017/60

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